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(54) HYDROGENATION OF POLYMERS

(71) We, BAYER AKTIENGESELLSCHAFT, of 509 Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 This invention relates to a process for the production of partially hydrogenated copolymers of an α,β -unsaturated carboxylic acid or derivatives thereof and a hydrocarbon containing conjugated double bonds. 5

Random copolymers of monomers such as these are known from German Patent Specifications Nos. 570,980 and 658,172. They are obtained by the emulsion copolymerisation of, for example, acrylonitrile with conjugated dienes, such as butadiene. 10

It is known from US-PS 3,700,637 that regularly alternating copolymers can be produced from butadiene and acrylonitrile and can be hydrogenated by means of rhodium complexes as catalysts with the nitrile groups left intact. 10

15 In the context of the present invention, copolymers are both regularly alternating and also random copolymers of an α,β -unsaturated carboxylic acid or derivative thereof and an unsaturated hydrocarbon containing conjugated double bonds. The back-bone of the copolymer consists entirely of carbon atoms. 15

Suitable carboxylic acids and their derivatives are, for example, (meth)acrylic acid, fumaric acid, their esters and amides, and also the corresponding carboxylic acid nitriles, such as (meth)acrylonitrile. Suitable conjugated dienes are, for example, butadiene, 20 isoprene, dimethyl butadiene and piperylene. The process according to the invention is preferably used for the partial hydrogenation of copolymers of (meth)acrylic acid or derivatives thereof and butadiene. Copolymers of 90 to 45% by weight of butadiene and 10 to 55% by weight of acrylonitrile (based in each case on the copolymer total) are particularly preferred. 25

-In addition to the functional groups emanating from the carboxylic acid or its derivatives, for example the nitrile group, unsaturated structural units present in the above-mentioned copolymers are the vinyl groups formed during 1,2-bonding of the dienes used and the cis- or trans-configuration olefinic double bonds formed during 1,4-bonding. 30

According to the invention, the copolymers are dissolved in suitable organic solvents and are hydrogenated in the presence of a rhodium complex and, optionally, a ligand of the complex, e.g. triphenyl phosphine, at elevated temperature and pressure with any other functional groups, e.g. the nitrile group, left intact. In this connection, it has surprisingly been found that, in cases where chlorobenzene is used as solvent, the vinyl groups and the trans-configuration double bonds in the above-mentioned copolymers are completely hydrogenated in a selective manner. If on the other hand other solvents are used, the vinyl groups are completely hydrogenated, whereas the trans-configuration double bonds are only partially hydrogenated. The degree of hydrogenation of the trans-configuration double bonds amounts to between 10 and 90 %, based on the quantity of these double bonds, depending upon the solvent used. It was by no means foreseeable to the expert that the controlled use of certain solvents in a hydrogenation reaction carried out under identical conditions would enable the vinyl groups to be completely hydrogenated and the trans-configuration double bond to be completely or partially hydrogenated in a selective manner. 35 40

45 The present invention relates to a process for selective hydrogenation of the vinyl groups 45

and trans-configuration double bonds in copolymers of an α,β -unsaturated carboxylic acid or a derivative thereof and an unsaturated hydrocarbon containing conjugated double bonds, the back-bone of the copolymer consisting entirely of carbon atoms, distinguished by the fact that a 1 to 20 % solution of the copolymer in a suitable organic solvent is hydrogenated at 50 to 150°C and at 5 to 300 atms (absolute pressure) in the presence of 0.01 to 10 % by weight of a catalyst of a complex compound of a monovalent or trivalent rhodium halide, and, optionally, 5 to 25 % by weight of the ligand bound in the complex (based in each case on dissolved copolymer). Selective hydrogenation of the vinyl groups and trans-configuration double bonds in the copolymers may be carried out in a chlorine-substituted aromatic solvent with from 6 to 12 carbon atoms, preferably chlorobenzene, as solvent. In this medium the polar groups (for example nitrile groups) do not undergo any demonstrable hydrogenation. If solutions of the copolymers in other solvents, such as for example toluene, benzene, xylene, dimethyl formamide, ethyl acetate, methyl ethyl ketone, tetrahydrofuran, cyclohexanone or methylene chloride, are used in accordance with the invention, complete hydrogenation of the vinyl groups is accompanied by only partial hydrogenation of the trans-configuration double bonds.

The degree of hydrogenation of these double bonds is governed by the type of solvent used and decreases from around 90 to about 10 % in the order benzene > dimethylformamide \approx xylene > ethyl acetate > toluene > methyl ethyl ketone > cyclohexanone > tetrahydrofuran > methylene chloride. Although not necessary, it is of course also possible to use solvent mixtures for the process according to the invention.

The solutions contain from 1 to 20 % by weight and preferably from 2.5 to 10 % by weight of the copolymers, based on the particular above-described solvent used for the process according to the invention.

From 0.01 to 10 % by weight and preferably from 0.1 to 5 % by weight (based on the dissolved copolymer) of a complex compound of monovalent or trivalent rhodium halides are added to the solutions of the copolymers as a catalyst for the hydrogenation reaction. Suitable complex compounds correspond to the general formula (I):



in which R = C_1-C_8 alkyl, C_6-C_{15} aryl or C_7-C_{15} aralkyl,

B = P, As, S or S=O,

X = Cl or Br,

m = 2 or 3, and

n = 1 or 3.

Preferred complex compounds of this type are tris-(triphenyl phosphine)-rhodium(I)-chloride, tris-(triphenyl phosphine)-rhodium(III)-chloride and tris-(dimethyl sulphoxide)-rhodium(III)-chloride.

The pressure under which the hydrogenation reaction according to the invention is carried out may be varied within a wide range. Suitable pressures are in the range of from 5 to 300 atms and preferably in the range of from 50 to 100 atms. The hydrogenation reaction is carried out at temperatures in the range of from 50 to 150°C, and preferably at temperatures in the range of from 75 to 115°C. Under these conditions, the selective hydrogenation reaction is over after about 3 to 7 hours.

The catalyst may be separated off by the method described in DT-AS 1,558,395.

The hydrogenation product is separated off from the reaction solution by treatment with steam or by pouring into methanol and is subsequently dried under reduced pressure at a temperature of approximately 70°C.

Qualitative and quantitative determination of the hydrogenated double bonds and double bonds still present in the copolymers hydrogenated in accordance with the invention is carried out by IR-spectroscopic analysis. For further characterisation the iodine number and the glass transition temperature of the hydrogenation products are determined (in case of the glass transition temperature by thermomechanical analysis (TMA) and shear modulus measurement).

The copolymers hydrogenated by the process according to the invention show increased tensile strength for increased elongation at break and, in addition, improved elasticity. They are vulcanisable rubbers which may be used as temperature-resistant materials, for example in the sealing field.

Three different acrylonitrile-butadiene copolymers are used in the following Examples. The percentages quoted are always per cent by weight.

The quantities of catalysts and triphenyl phosphine quoted in the Examples are based in each case on the dissolved copolymer.

Copolymer I: of 82% of butadiene and 18% of acrylonitrile
 Copolymer II: of 72% of butadiene and 28% of acrylonitrile
 Copolymer III: of 62% of butadiene and 38% of acrylonitrile
 (based in each case on the copolymer total).

Example 1

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer I in chlorobenzene, followed by hydrogenation for 5.5 hours at 100°C/60 atms.

On completion of hydrogenation, the catalyst is separated off in accordance with DT-AS 1,558,395. The reaction products are precipitated by pouring the reaction solution into methanol, and are subsequently dried under reduced pressure at approximately 70°C.

The hydrogenation product obtained has the following properties:

Degree of hydrogenation: 100% of the vinyl and 100% of the trans-double bonds

Glass transition temperature: $T_g = -31^\circ C$

Iodine Number: INo. = 14

The hydrogenation products of the following Examples are worked up and characterised in the same way as described in Example 1.

Example 2

1% of $[(C_6H_5)_3P] Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in chlorobenzene, followed by hydrogenation for 4.5 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

Degree of hydrogenation: 100% of the vinyl and 100% of the trans-double bonds

Glass transition temperature: $T_g = -30^\circ C$

Iodine Number: INo. = 26

Example 3

1% of $[(C_6H_5)_3P]_3 Rh^{III} Cl_3$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in chlorobenzene, followed by hydrogenation for 5.5 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

Degree of hydrogenation: 100% of the vinyl- and 100% of the trans-double bonds

Glass transition temperature: $T_g = -30^\circ C$

Iodine number: INo. = 22

Example 4

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer III in chlorobenzene, followed by hydrogenation for 6 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

Degree of hydrogenation: 100% of the vinyl- and 100% of the trans-double bonds

Glass transition temperature: $T_g = -27^\circ C$

Iodine Number: INo. = 22

Example 5

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer I in the toluene, followed by hydrogenation for 4.5 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

Degree of hydrogenation: 100% of the vinyl- and 48% of the trans-double bond

Glass transition temperature: $T_g = -43^\circ C$

Iodine Number: INo. = 50

Example 6

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in the toluene, followed by hydrogenation for 5.2 hours at 100°C/60 atms. The hydrogenation product has the following properties:

5	Degree of hydrogenation:	100% of the vinyl- and 42% of the trans-double bonds	5
	Glass transition temperature:	$T_g = -26^\circ C$	
10	Iodine Number:	INo. = 95	10

Example 7

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer III in toluene, followed by hydrogenation for 5 hours at 100°C/60 atms.

15	The hydrogenation product has the following properties:		15
	Degree of hydrogenation:	100% of the vinyl- and 30% of the trans-double bonds	
	Glass transition temperature:	$T_g = -26^\circ C$	
20	Iodine number:	INo. = 60	20

Example 8

1% of $[(CH_3)_2S=O]_3 Rh^{III} Cl_3$ and 10% of $(CH_3)_2S=O$ are added to a 2.5% solution of copolymer II in chlorobenzene, followed by hydrogenation for 7.5 hours at 100°C/60 atms. The hydrogenation product has the following properties:

	Degree of hydrogenation:	100% of the vinyl- and 100% of the trans-double bonds	
30	Glass transition temperature:	$T_g = -29^\circ C$	30
	Iodine number:	INo. = 29	

Example 9

1% of $[(C_6H_5)_3P]_3 Rh^{III} Cl_3$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in benzene, followed by hydrogenation for 6.2 hours at 100°C/60 atms. The hydrogenation product has the following properties:

40	Degree of hydrogenation:	100% of the vinyl- and 90% of the trans-double bonds	40
	Glass transition temperature:	$T_g = -30^\circ C$	
	Iodine number:	INo. = 19	

Example 10

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in ethyl acetate, followed by hydrogenation for 5.5 hours at 100°C/60 atms. The hydrogenation product has the following properties:

50	Degree of hydrogenation:	100% of the vinyl- and 50% of the trans-double bonds	50
	Glass transition temperature:	$T_g = -38^\circ C$	
	Iodine number:	INo. = 77	

Example 11

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in methyl ethyl ketone, followed by hydrogenation for 6 hours at 100°C/60 atms.

60	The hydrogenation product has the following properties:		60
	Degree of hydrogenation:	100% of the vinyl- and 40% of the trans-double bonds	
	Glass transition temperature:	$T_g = -39^\circ C$	
65	Iodine number:	INo. = 119	65

Example 12

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in xylene, followed by hydrogenation for 6.5 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

5	Degree of hydrogenation:	100% of the vinyl- and 59% of the trans-double bonds	5
	Glass transition temperature:	$T_g = -39^\circ C$	
10	Iodine number:	INo. = 73	10

Example 13

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in dimethyl formamide, followed by hydrogenation for 4 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

	Degree of hydrogenation:	100% of vinyl- and 59% of the trans-double bonds	
20	Glass transition temperature:	$T_g = -42^\circ C$	20
	Iodine number:	INo. = 144	

Example 14

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in cyclohexanone, followed by hydrogenation for 4 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

30	Degree of hydrogenation:	100% of vinyl- and 38% of the trans-double bonds	30
	Glass transition temperature:	$T_g = -41^\circ C$	
	Iodine number:	INo. = 114	

Example 15

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in tetrahydrofuran, followed by hydrogenation for 3.2 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

40	Degree of hydrogenation:	100% of the vinyl- and 31% of the trans-double bonds	40
	Glass transition temperature:	$T_g = -39^\circ C$	
	Iodine number:	INo. = 113	

Example 16

1% of $[(C_6H_5)_3P]_3 Rh^I Cl$ and 10% of $(C_6H_5)_3P$ are added to a 2.5% solution of copolymer II in methylene chloride, followed by hydrogenation for 6.5 hours at 100°C/60 atms.

The hydrogenation product has the following properties:

50	Degree of hydrogenation:	100% of the vinyl- and 12% of the trans-double bonds	50
	Glass transition temperature:	$T_g = -40^\circ C$	
55	Iodine number:	INo. = 160	55

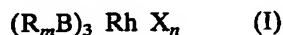
The results of Examples 1 to 16 are summarised in Table 1 below:

TABLE 1.

Example	Co-polymer	Solvent	Degree of hydrogenation(%) Catalyst	vinyl— trans-double bonds	T_g	INo.
1	I	chlorobenzene	$[(C_6H_5)_3P]_3Rh^I Cl$	100	-31	14
2	II	"	"	100	-30	26
3	II	"	$[(C_6H_5)_3P]_3Rh^{III} Cl_3$	100	-30	22
4	III	"	$[(C_6H_5)_3P]_3Rh^I Cl$	100	-27	22
5	I	toluene	"	100	-43	50
6	II	"	"	100	-26	95
7	III	"	"	100	-26	60
8	II	chlorobenzene	$[(CH_3)_2S=O]_3Rh^{III} Cl_3$	100	-29	29
9	II	benzene	$[(C_6H_5)_3P]_3Rh^{III} Cl_3$	100	-30	19
10	II	ethyl acetate	$[(C_6H_5)_3P]_3Rh^I Cl$	100	-38	77
11	II	methyl ethyl ketone	"	100	-39	119
12	II	xylene	"	100	-39	73
13	II	dimethyl formamide	"	100	-42	144
14	II	cyclohexanone	"	100	-41	114
15	II	tetrahydrofuran	"	100	-39	113
16	II	methylene chloride	"	100	-40	160

WHAT WE CLAIM IS:-

1. A process for the selective hydrogenation of the vinyl groups and trans-configuration double bonds in a copolymer of an α,β -unsaturated carboxylic acid or a derivative thereof and an unsaturated hydrocarbon containing conjugated double bonds, the back-bone of the copolymer consisting entirely of carbon atoms, which comprises hydrogenating a 1 to 20% solution of the copolymer in an organic solvent at a temperature of from 50 to 150°C and at pressure of from 5 to 300 atmospheres in the presence of from 0.01 to 10% by weight of a complex of a monovalent or trivalent rhodium halide as a catalyst and, optionally, from 5 to 25% by weight of the ligand bound in the complex (based in each case on the dissolved copolymer).
2. A process as claimed in Claim 1, wherein the solvent is a chlorine-substituted aromatic solvent with from 6 to 12 carbon atoms, and the vinyl groups and the trans-configuration double bonds are completely hydrogenated in a selective manner.
3. A process as claimed in Claim 1, wherein the solvent is toluene, benzene, ethyl acetate, methyl ethyl ketone, xylene, dimethyl formamide, cyclohexanone, tetrahydrofuran or methylene chloride, and from 10 and 90% of the trans-configuration double bonds, in addition to the vinyl groups, are hydrogenated, depending upon the solvent used.
4. A process as claimed in any of Claims 1 to 3, wherein the copolymer to be hydrogenated is a copolymer of (meth)acrylic acid, an ester or amide thereof or (meth)acrylonitrile, with butadiene, isoprene, dimethyl butadiene or piperylene.
5. A process as claimed in any of Claims 1 to 4, wherein the copolymer is a butadiene-acrylonitrile copolymer of from 90 to 45% by weight of butadiene and from 10 to 55% by weight of acrylonitrile (based in each case on the copolymer total).
6. A process as claimed in any of claims 1 to 5, wherein the complex corresponds to the general formula (I):



- in which R = C_1-C_8 alkyl, C_6-C_{15} aryl or C_7C_{15} aralkyl,
 B = P, As, S or S=O,
 X = Cl or Br,
 m = 2 or 3, and
 n = 1 or 3.
7. A process as claimed in any of Claims 1 to 6, wherein the hydrogenation is carried out in the presence of from 0.1 to 5% of the complex.
 8. A process as claimed in any of Claims 1 to 7, wherein the hydrogenation temperature is from 75 to 115°C.
 9. A process as claimed in any of Claims 1 to 8, wherein the hydrogenation pressure is from 50 to 100 atmospheres.
 10. A process as claimed in any of claims 1 to 9, wherein the rhodium complex has sulphur-containing ligands.
 11. A process as claimed in Claim 1, substantially as herein described with reference to any of the specific Examples.
 12. A copolymer when hydrogenated by a process as claimed in any of Claims 1 to 11.

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